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Attempted Oxidation of Benzaldehyde with Sodium Bismuthate (Part One). Reduction of Xanthene by Lithium in Methylamine (Part Two)

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Part One

ATTEMPTED OXIDATION OF BENZALDEHYDE WITH SODIUM BISMUTHATE

Part Two

REDUCTION OF XANTHENE BY LITHIUM IN METHYLAMINE

by

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Part One

Attempted Oxidation of Benzaldehyde With Sodium Bismuthate

Introduction

There have been several articles published concerning sodium bismuthate and its properties. Most of these however, dealt either with the preparation of, or an analytical procedure for, this reagent (1,2). It has been used in the determination of manganese in certain steels (it oxidizes the manganese to permanganate (3)). There have been very few articles published concerning the oxidation of organic compounds by this reagent. Brooks and Norymberski have used sodium bismuthate to characterize the group of corticosteroids bearing a dihydroxyacetone side chain. The sodium bismuthate converts these to 17-ketosteroids which are fairly easy to characterize and assay (4). Rigby has used sodium bismuthate to oxidized α,β-glycols and α-hydroxyketones(5). In these oxidations the bond between the two carbons which are attached to the oxygen atoms is cleaved and the products are aldehydes and/or ketones.

The purpose of this investigation was to determine whether sodium bismuthate would oxidize an aldehyde containing only one oxygen atom. Benzaldehyde

was selected for these studies because it is a relatively good reducing agent and is not likely to undergo condensation reactions.

Experimental Part

Standard solutions of ferrous sulfate in four normal sulfuric acid, and potassium dichromate were prepared. The sodium bismuthate was then assayed using a volumetric method given by Rigby (6) and Ami (2). The indicator used was diphenylamine-sulfonic acid. It was found that the "Baker Analyzed" sodium bismuthate had an oxidizing capacity equivalent to 89.5 - 90.0% $NaBiO_3$. This method of analysis was also tried on a known amount of sodium bismuthate and benzaldehyde in a mixture to see if the benzaldehyde interfered. It did not.

An attempt to run the oxidation of benzaldehyde in a homogeneous mixture failed because of the solubility behavior of sodium bismuthate. It would not dissolve in aqueous acetic acid, acetic acid with a small amount of sulfuric acid or in glacial acetic acid. Because of this, the kinetics of the reaction could not be followed and it was decided to run the reaction in a heterogeneous mixture with glacial acetic acid as the solvent, as Rigby had done

The first reaction mixture studied consisted of 0.0100 mole of sodium bismuthate, 0.0141 mole of benzaldehyde and 200 ml. of glacial acetic acid. The cloudy, orange-yellow reaction mixture was

stirred and heated to below its reflux temperature. After approximately two and one-half hours it was apparent that a reaction had occurred. The insoluble, quinquevalent bismuth had been reduced to soluble, trivalent bismuth as Rigby had previously observed (6). Freshly standardized ferrous sulfate solution was added to an aliquot of the product mixture and a volumetric analysis for Bi(V), similar to the one mentioned above was performed. This showed that 8.10 ± 0.01% of the original quinquevalent bismuth remained in the mixture. The product mixture was diluted with glacial acetic acid and absolute ethanol until it was approximately 1.25 x 10^{-2}M in bismuth and 1.76 x 10^{-2}M in benzaldehyde or benzoic acid. Ultra-violet absorption spectra of this solution and a solution which was 1.25 x 10^{-2}M in benzoic acid were taken. The spectra were not very enlightening and it was decided to run the reaction again and make the dilutions quantitatively.

It was decided to attempt the oxidation of benzaldehyde at room temperature. Two reaction mixtures were prepared. Both had 0.0100 mole of sodium bismuthate and 50 ml. of glacial acetic acid. However one also had 0.0100 mole of benzaldehyde. These mixtures were put in florence flasks and, after placing a cork with a small hole filed along

along the edge in each flask, the flasks were placed on a Burrell "Wrist Action" shaker. They were shaken for ten days at room temperature. At the end of this time the reaction mixture which had the benzaldehyde in it was light tan in colour with very little solid. This will hereafter be referred to as product number one. The other flask was orange-yellow in colour and there was still quite a bit of solid in it. Titrations revealed that 1.50% of the quinquevalent bismuth remained in flask one, while 12.40% remained in flask two. This is a difference of 10.90% in quinquevalent bismuth. Product number one was diluted with glacial acetic acid and absolute ethanol until it was 4.0×10^{-5}M in Bi(III) and benzaldehyde or benzoic acid and 0.20% in acetic acid. An ultra-violet absorption spectrum was taken of this solution. The spectrum is shown in figure one in the appendix.

A mixture of 0.0100 mole of sodium bismuthate, 0.0100 mole of benzaldehyde and 50 ml. of glacial acetic acid was prepared. It was stirred and heated, this time to reflux temperature. The contents of the flask were clear and light yellow in colour after seventeen minutes at reflux temperature. This mixture will be referred to as product number two. It was diluted with glacial acetic acid and absolute ethanol until it was 4.0×10^{-5}M in bismuth and

and benzaldehyde or benzoic acid and 0.20% in acetic acid. An ultra-violet absorption spectrum was taken of this diluted mixture (see figure two).

A mixture of 0.0300 mole of sodium bismuthate in 50 ml. of glacial acetic was prepared and heated to reflux temperature with stirring. From the change in appearance of the mixture, it was clear that the quinquevalent bismuth had been reduced to trivalent bismuth within fifty minutes (a comparable experiment had previously shown that homogenity can be reached after seventeen minutes at reflux and that no quinquevalent bismuth survives). This product will be referred to as Bi(III) for simplicity. It was diluted with glacial acetic acid and absolute ethanol until it was 6.0×10^{-5}M in bismuth and 0.10% in acetic acid. An ultra-violet absorption spectrum was taken of this solution and may be seen in figure three.

Solutions which were 6.0×10^{-5}M in benzoic acid (0.02% acetic acid) and 6.4×10^{-5}M in benzaldehyde were prepared. The major solvent in all cases was absolute ethanol, but it was necessary to use acetic acid in the first stages of the dilutions of solutions containing bismuth to prevent the bismuth from precipitating out of solution. Ultra-violet absorption spectra of the above solutions were taken and may be seen in figure three.

Solutions which were 0.20%, 0.10% and 0.05% in acetic acid were also prepared and ultra-violet absorption spectra taken. These spectra are not shown in the appendix because they were merely used to correct the other spectra for acetic acid absorption. In addition, 1:1 mixtures of the dilution of Bi(III) and benzoic acid and Bi(III) and benzaldehyde were prepared and ultra-violet absorption spectra were taken. These spectra are shown in figure four.

Analysis of Data

Since the concentrations of the solutions used in the spectroscopic studies varied, the molar absorptivities (hereafter represented by ε) were calculated for benzoic acid, benzaldehyde and and the Bi(III) solutions. This was done by dividing the absorbance of each solution, corrected for acetic acid, at five millimicron intervals, from 240mμ to 300mμ, by the concentration of that solution. These values of ε are shown in table one in the appendix. Using these values the absorbances of the two known mixtures were calculated. Thus there are two values of the absorbances for the mixtures, an experimentally determined one and one calculated from the molar absorptivities of the dissolved solutes. These values are tabulated in table two at 5mμ intervals. From these values apparent molar absorptivities for (Bi(III) and

benzoic acid) and (Bi(III) and benzaldehyde) were determined, and these values are shown in table three. The experimental values of ε for products one and two were determined using figures one and two and a value of 4.0×10^{-5}M for the concentration of either component, Bi(III) and benzoic acid or benzaldehyde. These values are shown in table four.

Then the percentages of the observed and calculated values of ε for the known mixtures which, when added together, would equal the values of ε for products one and two were determined. These percentages are shown in table five.

Results and Conclusions

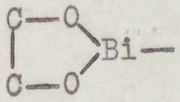
The values given in table five do not show any consistency as wavelength varies for a given set of values. The only set of values in table five which offers any degree of consistency is that for product two, and the consistency prevails only when the calculated percentages are based on the experimentally measured absorptivities for the solutions of (Bi(III) and benzoic acid) and (Bi(III) and benzaldehyde) (columns eight and nine). This inconsistency obviously makes the quantitative interpretation of the spectroscopic data impossible. There may have been some species other than benzoic acid, benzaldehyde and bismuth ion present in the mixtures which was not accounted for and caused this inconsistency

Nevertheless it seems as if some of the benzaldehyde has been oxidized to benzoic acid in the reactions. The amount cannot be very large since the spectra of the products and the mixture (Bi(III) and benzaldehyde) are so similar. Also, the percentage of the benzoic acid mixture required in table five for the one set of consistent values never rises above forty per-cent (column eight). Some benzaldehyde may have been oxidized in the reactions but the amount of such oxidation was not very large and the benzoic acid resulting from such oxidation could not be proven, absolutely, to be in the product mixtures.

Earlier, it was stated that when Bi(V) was separately suspended in acetic acid that contained an equivalent of benzaldehyde and also in acetic acid alone, almost all of the Bi(V) had reacted in the presence of benzaldehyde but only 10.9% more than in the absence of benzaldehyde. As the spectrum of product one (figure one) and calculated percentages (table five, columns 2-5) show, not very much benzoic acid is present in the product mixture. Thus, even though the quinquevalent bismuth ion concentration equaled the benzaldehyde concentration at the start of this reaction, apparently little benzaldehyde was oxidized. What was, could have been oxidized by the oxygen in air since the flasks were open for ten days (this time being required for the reaction to take place).

This study implies, albeit qualitatively, that sodium bismuthate is not reduced to an appreciable extent by benzaldehyde. Certainly the oxidizing agent in the reactions described by Rigby is bismuthic acid: $HBiO_3$. The oxidations he describes were all run in an acidic medium (either glacial acetic or phosphoric acid) and an acidic medium is necessary for Bi(V) to act as an oxidizing agent. Bismuthic acid is unstable in phosphoric and sulfuric acid solutions and decomposes spontaneously, with effervescence, to a Bi(III) species (7). The reducing agent must compete with this spontaneous decomposition of the quinquevalent bismuth, in order to become oxidized.

Rigby proposes the existence of a cyclic intermediate between bismuth and the two carbonyl oxygen atoms during the oxidation of the compounds he studied (I). If a cyclic intermediate is required



(I)

to compete with the spontaneous decomposition of bismuthic acid, benzaldehyde or any other mono-carbonyl compound would not be oxidized by sodium bismuthate.

Suggestions for Further Work

There is really very little that can be done with this phase of the study of the oxidizing properties of sodium bismuthate. Development of a good analytical procedure for the product mixtures would be quite helpful. Perhaps a polarographic means of analysis could be developed.

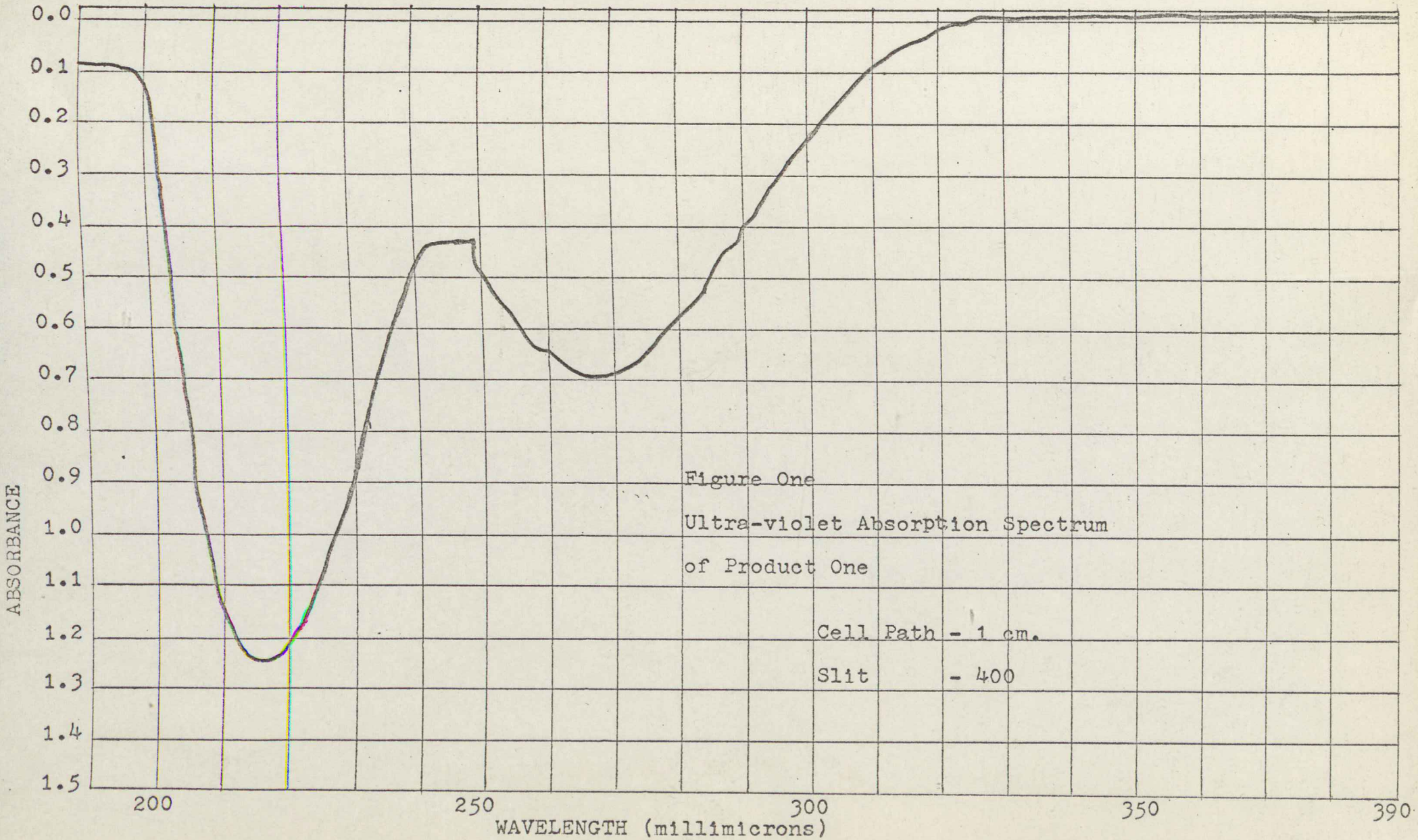


Figure One

Ultra-violet Absorption Spectrum

of Product One

Cell Path - 1 cm.

Slit - 400

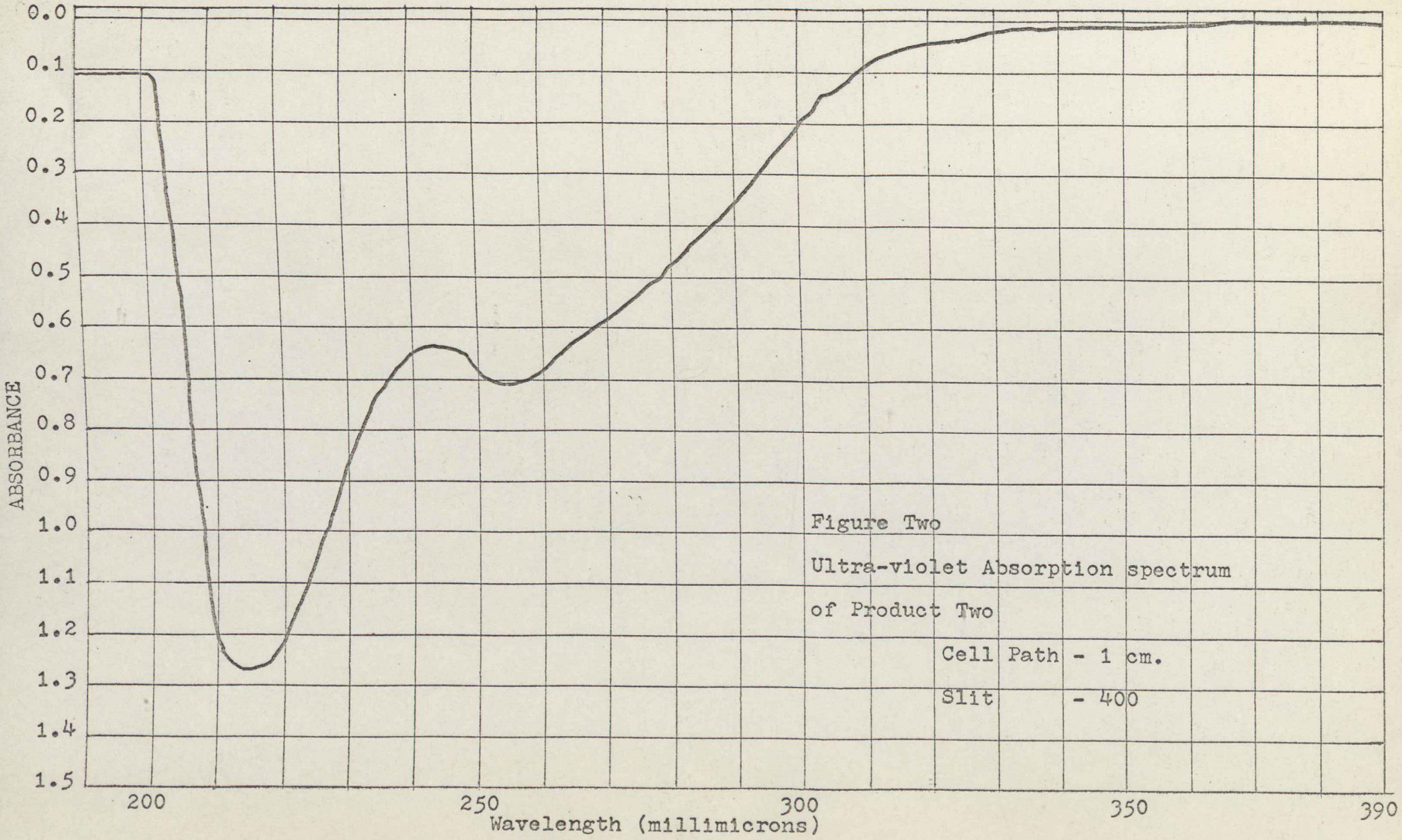


Figure Two

Ultra-violet Absorption spectrum of Product Two

Cell Path - 1 cm.

Slit - 400

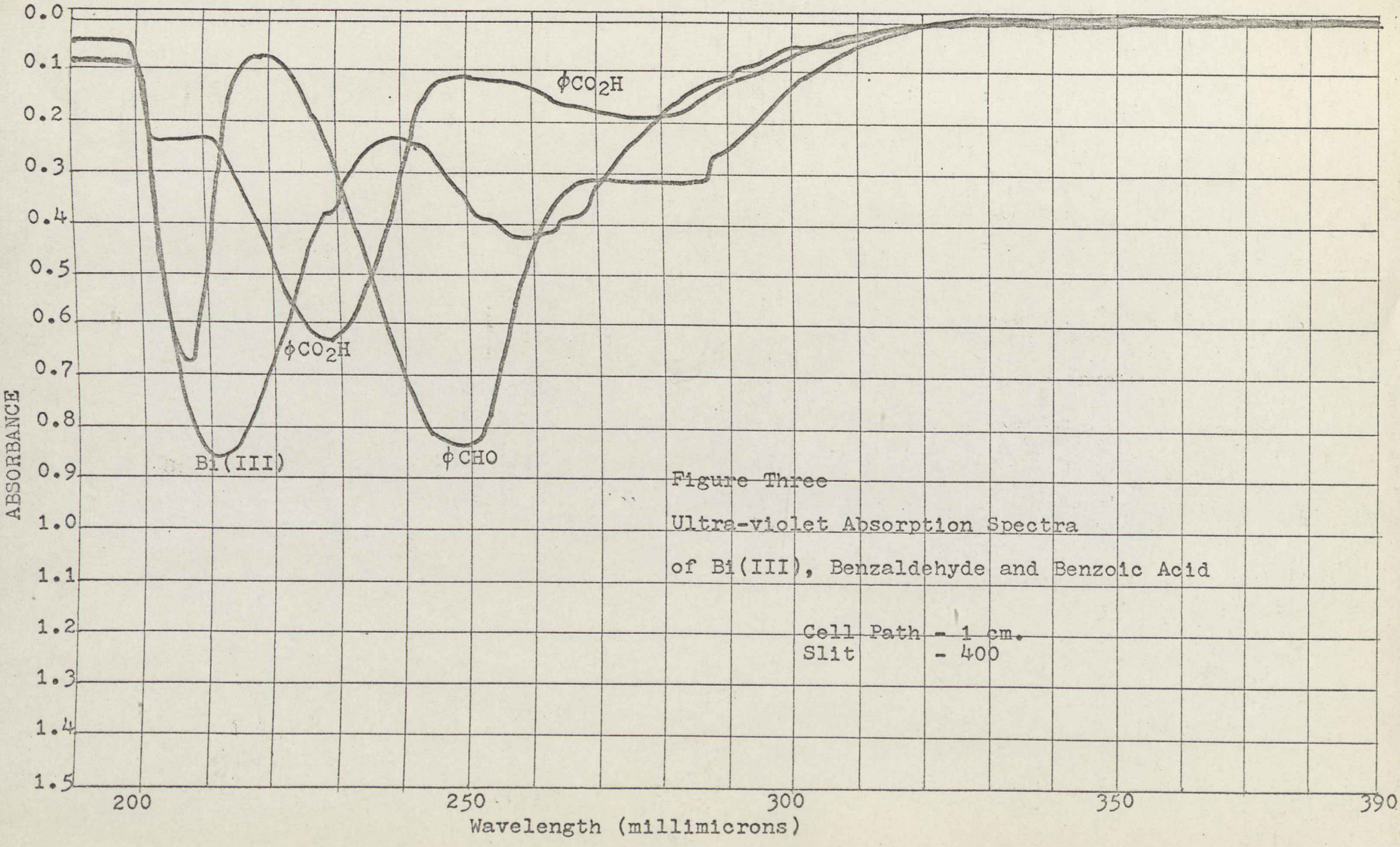


Figure Three

Ultra-violet Absorption Spectra

of Bi(III), Benzaldehyde and Benzoic Acid

Cell Path - 1 cm.
Slit - 400

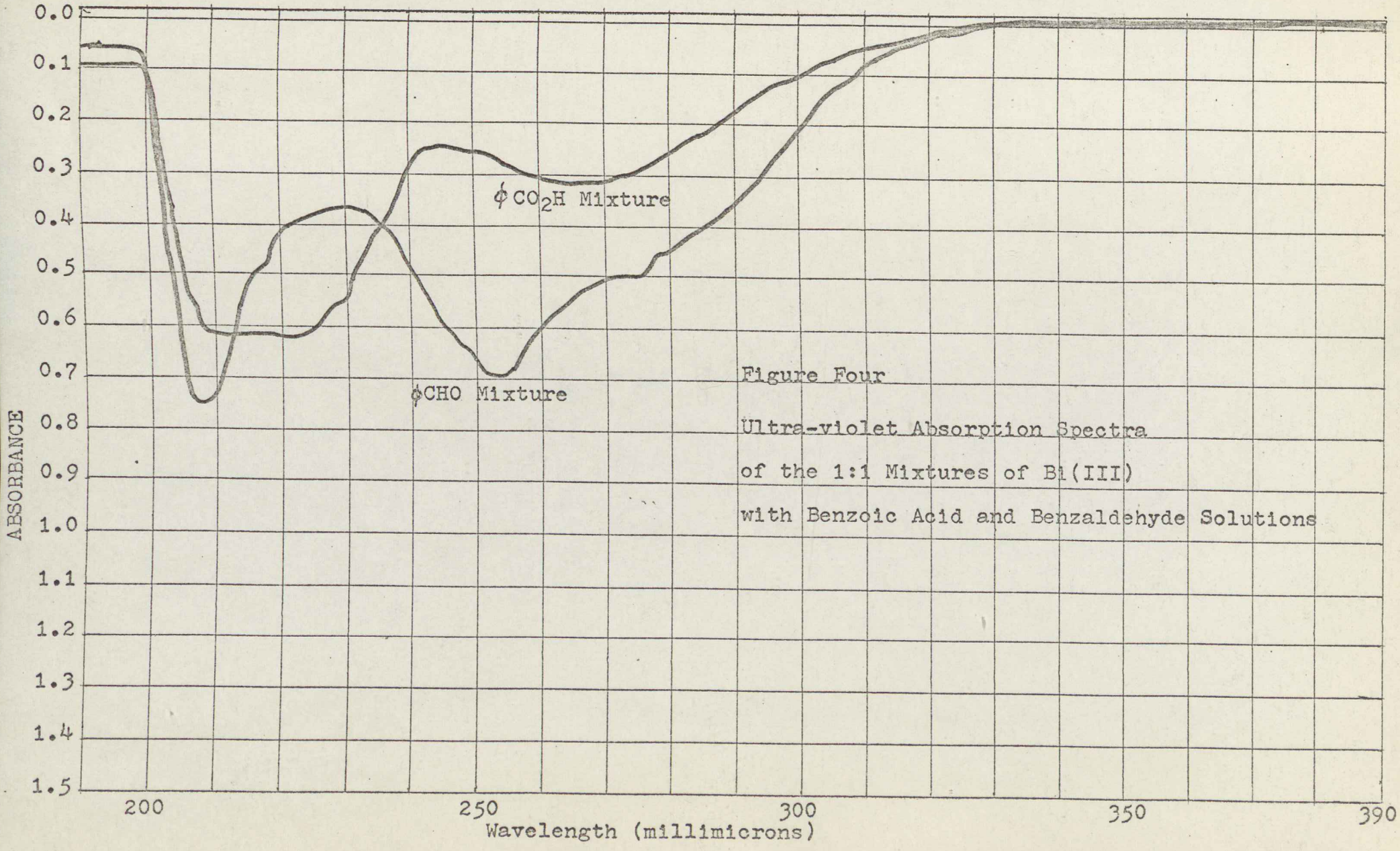


Figure Four

Ultra-violet Absorption Spectra

of the 1:1 Mixtures of Bi(III)

with Benzoic Acid and Benzaldehyde Solutions

Table One

Values of ε for Benzoic acid, Benzaldehyde and Bi(III) (values x 10^{-4})

λ(mμ)	Benzoic Acid	Benzaldehyde	Bi(III)
240	0.492	0.275	1.09
245	0.208	0.392	1.27
250	0.183	0.542	1.29
255	0.192	0.625	1.02
260	0.255	0.650	0.695
265	0.267	0.592	0.531
270	0.292	0.492	0.493
275	0.317	0.367	0.493
285	0.275	0.167	0.485
290	0.209	0.117	0.391
295	0.175	0.083	0.297
300	0.125	0.033	0.187

Values of ε_{Max} for Benzaldehyde and Benzoic acid taken from- Silverstein and Bassler, Spectrometric Identification of Organic Compounds, Wiley, New York, 1964, Page 101

Benzaldehyde - 1,500 at 280mμ, solvent- alcohol

Benzoic Acid - 800 at 270mμ, solvent- water

Table Two

Observed (obs.) and Calculated (calc.) values of Absorbance (A) for the known 1:1 mixtures of Bi(III) with benzoic acid and benzaldehyde solutions

	Bi(III) and ϕCO_2H		Bi(III) and ϕ CHO	
λ(mμ)	A calc.	A obs.	A calc.	A obs.
240	0.231	0.235	0.432	0.450
245	0.180	0.215	0.524	0.575
250	0.218	0.235	0.577	0.655
255	0.246	0.260	0.514	0.665
260	0.263	0.285	0.417	0.570
265	0.257	0.285	0.348	0.505
270	0.236	0.280	0.306	0.465
275	0.205	0.250	0.268	0.460
280	0.170	0.215	0.236	0.405
285	0.133	0.175	0.205	0.360
290	0.097	0.130	0.160	0.305
295	0.078	0.095	0.123	0.235
300	0.048	0.080	0.072	0.160

Table Three

Observed (obs.) and Calculated (calc.) values of molar absorptivity for the known mixtures of Bi(III) with Benzoic acid and Benzaldehyde solutions (x 10-4).

	Bi(III) and ϕCO_2H		Bi(III) and ϕCHO	
λ(mμ)	calc.	obs.	calc.	obs.
240	0.770	0.783	1.43	1.50
245	0.600	0.717	1.75	1.92
250	0.727	0.783	1.92	2.18
255	0.820	0.867	1.71	2.22
260	0.877	0.950	1.39	1.90
265	0.857	0.950	1.16	1.68
270	0.787	0.933	1.02	1.55
275	0.683	0.833	0.893	1.53
280	0.567	0.717	0.787	1.35
285	0.443	0.583	0.683	1.20
290	0.310	0.433	0.533	1.02
295	0.260	0.317	0.410	0.783
300	0.160	0.267	0.240	0.533

Table Four

Experimental values of molar absorptivity for products one and two. (values x 10^{-4})

λ(mμ)	Product One	Product Two
240	0.963	1.37
245	0.987	1.50
250	1.07	1.64
255	1.38	1.70
260	1.56	1.65
265	1.64	1.50
270	1.64	1.37
275	1.51	1.26
280	1.36	1.10
285	1.15	0.950
290	0.937	0.800
295	0.725	0.612
300	0.525	0.437

Table Five

Percentages of calculated and observed values of molar absorptivity (ε) for the 1:1 mixtures which, when added together, equal the values of ε for the products

	Product One				Product Two			
	From calc.		From obs.		From calc.		From obs.	
λ(mμ)	%ϕCO$_2$H	%ϕCHO	%ϕCO$_2$H	%ϕCHO	%ϕCO$_2$H	%ϕCHO	%ϕCO$_2$H	%ϕCHO
240	71	29	74	26	09	91	18	82
245	66	34	78	22	21	79	35	65
250	71	29	79	21	23	77	39	61
255	37	63	62	38	01	99	38	62
260	Total over 100%		36	64	Total over 100%		26	74
265			06	94			25	75
270			10	100			29	71
275			03	97			39	61
280			01	100			40	60
285			08	92			40	60
290			14	86			37	63
295			12	88			37	63
300			03	97			36	64

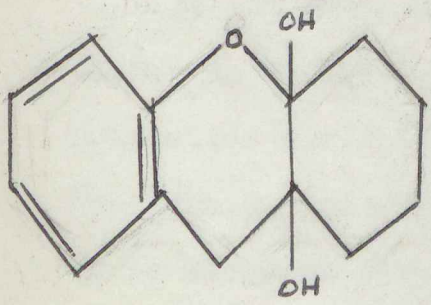
Part Two

Reduction of Xanthene By Lithium In Methylamine

Introduction

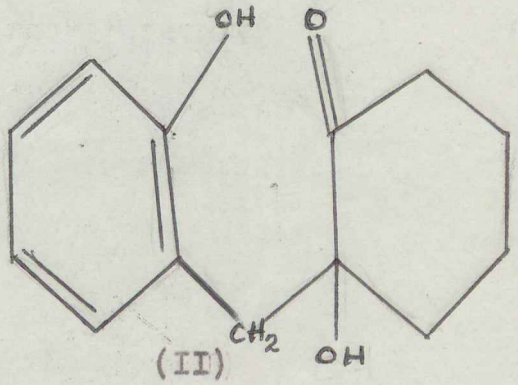
In 1952 Benkeser and co-workers reported that aromatic compounds took up a large amount of lithium in an ethylamine solvent system (8). They later reported (9,10) that, using such a system, aromatic compounds could be reduced to monoölefins.

Nielsen has investigated the reduction of fluorene by this method. He found that the reduction product is 1,2,3,4-tetrahydrofluorene but that the product resulting from its subsequent oxidation by performic acid is not the expected diol. It is instead a compound with the molecular formula, $C_{13}H_{18}O_3$ (11). He prepared several derivatives of this "trioxide" and also compared its infra-red spectrum with the spectra of oxidized fluorene, indene, and 1,2,-diethylindene. From this work, he proposed the structures shown below for the oxidation product of 1,2,3,4-tetrahydrofluorene (12).



(I)

And/Or



(II)

The compound (I), which Nielsen proposes as the form that exists in the solid state, is 1,2,3,4-tetrahydro-4a,9a-dihydroxyxanthene. It seemed that this compound could be synthesized by reducing xanthene to 1,2,3,4-tetrahydroxanthene and then oxidizing this reduction product with performic acid. If so, this offers an alternative route that can serve as confirmation of Nielsen's proposal for the product obtained from the successive reduction and oxidation of fluorene.

There have been some reports of compounds related to xanthene being reduced. In one case, 2,2'-dioxodicyclohexylmethane was reduced to 1,2,3,4,4a,5,6,7,8,9a-decahydroxanthene (13). The reduction of dihydroanthranol is reported to yield xanthene (14) and the reduction of xanthone yields hexa- or dodecahydroxanthene (15). There is also one report of a reaction between saligenol and cyclohexanone which yields 1,2,3,4-tetrahydro-4a-hydroxyxanthene (16).

It was also thought that if 5,6,7,8-tetrahydro-4a,8a-dihydroxybenzopyran could be synthesized, its properties would be similar to those reported for (I). There were, however, no references to this compound or to the reduction of benzopyran in the literature, from 1926 to the present. There was also no reference to it in Beilstein.

An inquiry was made to Dr. Benkeser and it revealed that neither he, nor anyone in his group, has attempted the reduction of xanthene using the lithium-low molecular weight amine system.

To summarize, the primary objective of this research is to confirm Nielsen's proposal that (I) and/or (II) is the oxidation product of 1,2,3,4-tetrahydrofluorene. In doing so, this project is also concerned with the attempted reduction of xanthene and the subsequent oxidation of its reduction product.

Experimental Part.

The xanthene obtained from Aldrich Chemicals was deemed sufficiently pure, with a melting point of 97.5-98.5 °C, to be used in these studies without further purification. Lithium in the form of a wire with a density of 0.043g./cm. was used in this work. Since the weight of the wire per centimeter was known, portions could be measured with a ruler and immediately added to the reaction mixture. This eliminated the possibility of oxidation of the metal or nitride formation taking place.

Xanthene (9.839 g., 0.054 mole) was placed in a three-necked flask equipped with a stirrer, a dry-ice condenser and a drying tube. The lecture bottle of methylamine used in these studies,

was cooled in dry-ice and then 100ml. (2.47 moles) of the methylamine was added to the reaction flask. This mixture was stirred and the methylamine allowed to reflux. Over a period of forty-five minutes, four portions of lithium wire totalling 2.42 grams (0.349 g. atom) were added to the mixture. When the first portion was added, a green colour was observed in the heterogeneous mixture. It gradually faded, and when it had disappeared the second portion was added. The green colour appeared again, but this time the reaction mixture turned to a dark red colour which did not fade. The mixture was stirred for approximately eight hours after the addition of the last portion of lithium.

The methylamine was allowed to evaporate and then 110ml. of water were added. A white precipitate, possibly lithium hydroxide, and a red oil appeared upon adding the water. The solution was made acidic with 40ml. of concentrated hydrochloric acid and the white precipitate dissolved.

The mixture was then extracted with three 50ml. portions of benzene. Both the benzene and the water layers were saved. Fifty milliliters of ethanol were added to the benzene layer and the solvent evaporated in a rotary evaporator. This was repeated three times but there was no precipitation when cool ethanol was added to the

evaporated mixture.

Thin layer chromatography was used to determine how many components were in the mixture. This was done on silica gel, using a 1:1 mixture of benzene and 65°-75°C boiling ligroin as the solvent. Three components were observed after developing the chromatograph with iodine. Upon running a thin layer chromatograph of the mixture and xanthene on the same plate, it was found that one of these components was probably unreacted xanthene.

Since thin layer chromatography on silica gel had separated the mixture so well, it was decided to attempt a separation on a larger scale, using a silica gel column. A column of silicic acid which was approximately 50cm. long was prepared in a 50ml. burette. One gram of the reaction mixture was added at the top of the column and then a 1:1 mixture of benzene and ligroin was passed through it. When less than 100ml. of the solvent had passed through, the components had separated into three distinct bands. The first band was eluted and attempts were made to recrystallize the compound, which was assumed to be xanthene. Some trouble was encountered in this recrystallization and, because there was no time remaining to continue the work, the compound was never successfully recrystallized. The other two bands were also not eluted because of the time factor.

Conclusions

There is little that can be concluded from the work described above. It is obvious from the colour changes and the chromatographic work that some sort of reaction involving the lithium-methylamine system and xanthene has taken place. From Benkeser's work, this reaction must have been a reduction but there were at least two compounds produced in this reduction and it is not known what they are.

Suggestions For Further Work

Nielsen's proposal has not been confirmed in this research and it is still not known positively, whether xanthene is reduced by lithium in methylamine

The reaction mentioned above must be studied again. The three components of the product mixture can be separated on a considerably shorter column than the one used in this work. This would reduce the time necessary to effect the separation and elution of the products. After the compounds have been separated and purified, studies of their infra-red and nuclear magnetic resonance spectra should lead to the identification of the reduction products. If one of these is 1,2,3,4-tetrahydroxanthene, it should then be oxidized by performic acid and the properties of the product determined. If they agree with those Nielsen gives in his thesis for (I), and if the infra-red and N.M.R. spectra indicate

that it is 1,2,3,4-tetrahydro-4a,9a-dihydroxyxanthene, then Nielsen's proposal will have been confirmed.

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